Internal Cyclization during Dediazoniation of 2,5-Bis(1,1,2,2-tetramethylpropyl)benzenediazonium Ion

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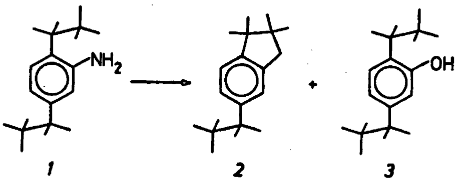
The synthesis of 2-amino-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*1*) was recently published.[1] It has been reported that thermal decomposition of *ortho*- alkylbenzenediazonium ions can result in internal ring closure reactions.[2,3] Thus the thermal decomposition of the diazonium ion derived from *1* has now been studied.

A product composition consisting of 93 % of 1,1,2,2-tetramethyl-5-1′,1′,2′,2′-tetramethylpropylindane (*2*) and 7 % of 2-hydroxy-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*3*) was obtained when the diazonium ion derived from *1* was thermally decomposed in 3 N sulfuric acid. In order to make a comparison with and confirm previous results,[2] those experiments were repeated under the present experimental conditions. The results are presented in Table 1. The formation of 13 % of indane and 35 % of 2-methylindane from *ortho*-propylaniline and *ortho*-isobutylaniline, respectively, along with the corresponding phenols was confirmed. *ortho*-Neopentylaniline was shown to give 83 % of 2,2-dimethylindane and 17 % of *ortho*-neopentylphenol. Since *ortho*-neopentylphenol[4] was not isolated in the previous study[2] its structure was established by its mass and ^{1}H NMR spectrum. The difference in product composition from the earlier report on the thermal decomposition of *ortho*-neopentylbenzenediazonium ion in 18 N sulfuric acid[2] can probably be explained by the formation of a mixture of *ortho*-neopentylphenol and different coupling products which were at that time not characterized. The formation of such coupling products (diaryl ethers and diaryl sulfates) are often found in thermal decompositions in acid solution[5] and may be minimized by decomposition in large volumes of dilute acid solution.[6]



1 *2* *3*

In dediazoniations of *ortho*-alkylsubstituted diazonium ions steric bulk of the alkyl groups clearly plays an important role in the product-forming step. The bulkiness of the 1,1,2,2-tetramethylpropyl (triptyl) group in electrophilic aromatic substitutions has been demonstrated,[1] and it is also shown in nucleophilic substitution, as *1* clearly yields less phenolic product (Table 1) in dediazoniation of the corresponding diazonium ion than does *ortho*-neopentylaniline.

In a report[3] regarding dediazoniation of the diazonium ion from 3-amino-4-*tert*-butyl-5-nitrobenzoic acid, ring closure yielding a benzocyclobutene derivative was found. As *1* can be viewed as a substituted *ortho*-*tert*-butylbenzene derivative a careful search was made in order to detect any benzocyclobutene derivative but none was found. The only minor product (less than 1 %) formed in the thermolysis of *1* had a mass spectrum with a nominal mass incompatible with a benzocyclobutene derivative. ^{1}H NMR spectroscopic studies of the 1,4-bis(1,1,2,2-tetramethylpropyl)benzene system have been discussed under the assumption that in the favoured conformation the triptyl groups are perpendicular to the aromatic ring.[1] This means that the α-methyl groups are not in the most favoured conformation for ring closure to a benzocyclobutene derivative. Knight *et al.* observed that in their system the buttressing effect of the 5-nitro group was necessary to get ring formation. The nitro group probably increases the population of a conformation with one of the α-methyl groups in the ring plane close to the diazonium group.

The thermal decomposition of arenediazonium ions in acidic aqueous solution is now generally believed to proceed by heterolysis[7] with formation of phenyl cations. The absence of any considerable amounts of by-products (Table 1) in the thermolysis of *ortho*-alkylsubstituted benzene diazonium ions strongly indicates that intramolecular cyclization does not occur *via* the formation of a primary aliphatic carbocation by a 1,5-hydride ion shift from a β-methyl group in the side chain of the initially formed phenyl cation. Such 1,5-hydrogen shifts are known to occur in cases where resonance stabilization is involved.[8] Also, in the special case of benzylic hydrogens the formation of a so-called pentacoordinated carbocation is discussed.[9] A similar type of intramolecular cyclization has been reported[10] in the acid catalyzed cleavage of 2,4,6-tri-*tert*-butylbenzyl methyl ether. Moreover, formation in the gas phase of primary aliphatic carbocations is known to be almost as difficult as formation of phenyl cations[11] so the most relevant explanation seems to be a direct attack by a phenyl cation on the alkyl side chain.

Experimental. GLC analyses were performed with a Perkin-Elmer 3920 gas chromatograph equipped with flame ionization detectors and 2

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Table 1. Dediazoniation of *o*-alkylbenzenediazonium ions in 3 N sulfuric acid.

Alkyl group	Product composition (%) Indane	Phenol	Total product yield (%)
Propyl	13	87	94
Isobutyl	35	65	92
Neopentyl	83	17	90
Triptyl	93	7	91

m packed columns (3 % SE-30) and a Hewlett-Packard 3380 A integrating recorder. The validity of the GLC analysis method was checked with an equimolar mixture of authentic 2-methylindane and *ortho*-isobutylphenol, showing equal responses on the particular detector used. This is also assumed to hold for the other compounds investigated. Mass spectra were recorded with an LKB 9000 instrument fitted with a gas chromatograph (at the Department of Medical Chemistry of Göteborg) using the same stationary phase and ^1H NMR spectra were recorded on a Bruker WH 270 instrument operating at 270 MHz.

Diazotization and thermal decomposition. To a stirred, cooled (−5 °C) suspension of *1* in 6 N sulfuric acid an equimolar amount of sodium nitrite in aqueous solution was added in small portions. Stirring was continued at that temperature for 45 min whereupon the reaction mixture (a white precipitate was present during the whole reaction) was poured into boiling 3 N sulfuric acid. The mixture was boiled for 10 min, cooled, diluted with aqueous sodium chloride and extracted with ether. The remaining water phase was made alkaline and ether extracted. No starting material could be found in the latter ether extract.

After the usual work-up procedure, the remaining crystalline residue was shown by GLC to be a mixture of two compounds in a ratio of 93:7, based on normalized peak-area values. These two compounds were identified by GLC-MS as 1,1,2,2-tetramethyl-5-1′,1′,2′,2′-tetramethylpropylindane (*2*) and 2-hydroxy-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (*3*), respectively. Recrystallization of the crude material (from methanol) yielded pure *2*, m.p. 126−127 °C. MS [IP 70 eV; *m/e* (rel.-int.)]:272(0.2), 216 (100), 214(6), 200(6), 185(16), 131(5), 91(24), 57(8), 41(11). NMR (270 MHz, $CDCl_3$): δ 0.83 (9H, s, *tert*-butyl), 0.96 (6H, s, 2,2-dimethyl), 1.07 (6H, s, 1,1-dimethyl), 1.33 (6H, s, 1′,1′-dimethyl), 2.66 (2H, s, methylene), 6.98 (1H, d, *J 8.1* Hz, aromatic), 7.14 (1H, s, aromatic), 7.16 (1H, d, *J* 8.1 Hz, aromatic).

MS of compound *3* [IP 70 eV; *m/e* (rel.-int.)]:290(0.3), 275(2), 233(74), 177(100), 176(16), 175(11), 161(12), 149(10), 133(5), 107(5), 91(4), 57(24), 41(19).

Identification of o-*neopentylphenol.* Separation of *o*-neopentylphenol from 2,2-dimethylindane in the reaction mixture from the thermal decomposition of *o*-neopentylbenzenediazonium ion was achieved by preparative TLC on silica gel using hexane-EtOAc (20:1 v/v) as eluent. The pure *o*-neopentylphenol had the following spectral characteristics. MS [IP 70 eV; *m/e* (rel.int.)]: 164(25), 149(10), 108(100), 107(65), 91(8), 79(11), 77(25), 57(82), 41(25). NMR (270 MHz, $CDCl_3$): δ 0.95 (9H, s, *tert*-butyl), 2.52 (2H, s, methylene), 4.81 (1H, s, OH), 6.95 (4H, m, aromatic).

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